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IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF :
YOSHIYUKI TANIGUCHI, ET AL. : EXAMINER: HAILEY, PATRICIA L.
SERIAL NO: 10/542,018 :
FILED: JULY 11, 2005 : GROUP ART UNIT: 1793
FOR: METHOD FOR PRESERVING :
CATALYST :

LETTER TO PERFECT PRIORITY

COMMISSIONER FOR PATENTS
ALEXANDRIA, VIRGINIA 22313

SIR:

Further to the Amendment filed concurrently herewith, Applicant submits herewith a certified English translation of the Japanese priority application (No. 2003-003115) to perfect priority in this case.

Applicant believes that the present application is in condition for allowance. Prompt and favorable consideration is earnestly solicited.

Respectfully submitted,

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Japanese Application of

Yoshiyuki TANIGUCHI, et al.

Japanese Patent Application No.: 2003-003115

Japanese Patent Filing Date: January 9, 2003

for: "METHOD FOR PRESERVING CATALYST"

VERIFICATION OF TRANSLATION

Honorable Commissioner of Patents and Trademarks

Washington, D.C. 20231

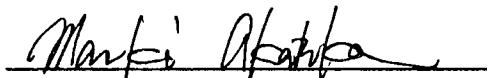
Sir:

Masaki AKATSUKA residing at 16th Kowa Bldg. No. 9-20 Akasaka 1-Chome, Minato-ku, Tokyo, Japan, declares:

- (1) that he knows well both the Japanese and English languages;
- (2) that he translated the above-identified Japanese Application from Japanese to English;
- (3) that the attached English translation is a true and correct translation of the above-identified Japanese Application to the best of his knowledge and belief; and
- (4) that all statements made of his own knowledge are true and that all statements made on information and belief and believed to be true, and further that these statements are made with the knowledge that willful false statements and the like are punishable by fine or imprisonment, or both, under 18 USC 1001, and that such false statements may jeopardize the validity of the application or any patent issuing thereof.

February 19, 2008

Date



Masaki AKATSUKA

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[Material Name] Specification 1
[Material Name] Abstract 1
[Proof] Requested

[Document Name] Specification

[Title of the Invention] Method for Preserving Catalyst

[Claims]

[Claim 1] A method for preserving a catalyst comprising maintaining a phosphorus-molybdenum-vanadium catalyst containing phosphorus, molybdenum and vanadium retained in a reactor under a condition of a water content of 30 mg or less per 1 g of catalyst dry weight, before the start of the reaction or during the stop of the reaction.

[Claim 2] The method for preserving a catalyst according to Claim 1, wherein a retaining temperature of said catalyst is 15 °C or higher and 150 °C or lower and a water concentration in gas in said reactor is 0.5 vol% or less.

[Claim 3] The method for preserving a catalyst according to Claim 2, wherein said temperature of the catalyst is retained 15 °C or higher and not higher than 150 °C, and the gas having a water concentration of 0.5 vol% or less and containing substantially no component lowering a catalytic performance is allowed to pass through in said reactor.

[Claim 4] The method for preserving a catalyst according to Claim 3, wherein the gas to be passed through in the reactor is an inert gas or oxidizing gas.

[Claim 5] The method for preserving a catalyst according to any one of Claims 1 to 4, wherein said phosphorus-molybdenum-vanadium catalyst is a catalyst used in producing methacrylic acid from methacrolein by catalytic oxidation in a vapor phase.

[Claim 6] The method for preserving a catalyst according to any one of Claims 1 to 5, wherein said phosphorus-molybdenum-vanadium catalyst is represented by the following formula (I):



wherein, P, Mo, V, Cu and O represent phosphorus, molybdenum, vanadium, copper and oxygen, respectively; X represents at least one element selected from the group consisting of antimony, bismuth, arsenic, germanium, zirconium, tellurium, silver, selenium, silicon, tungsten and boron; Y represents at least one element selected from the group consisting of iron, zinc, chromium, magnesium, tantalum, cobalt, manganese, barium, gallium, cerium and lanthanum; and Z represents at least one element selected from the group consisting of potassium, rubidium and cesium. a, b, c, d, e, f, g and h represent atom ratio of each element, and when b=12, then, a=0.5 to 3, c=0.01 to 3, d=0.01 to 2, e=0 to 3, f=0 to 3, g=0.01 to 3, and h represents atom ratio of oxygen necessary for satisfying atomic valence of each component.

[Claim 7] The method for preserving a catalyst according to any one of Claims 1 to 6, wherein said phosphorus-molybdenum-vanadium catalyst is preserved in dark ambient.

[Detailed Explanation of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to a method for preserving a catalyst, more specifically, in a process for continuously producing an objective product by a vapor phase oxidation reaction using a phosphorus-molybdenum-vanadium catalyst, to a method for preserving the catalyst with preventing the deterioration after filling a reactor with a catalyst or during the stop of operation.

[0002]

[Prior Art]

Conventionally, a phosphorus-molybdenum-vanadium catalyst containing phosphorus, molybdenum and vanadium is used in a method for producing methacrylic acid from methacrolein by catalytic oxidation in a vapor

phase, and other methods. Industrially, the phosphorus-molybdenum-vanadium catalyst is filled in a multi-tubular heat exchange type reactor, and methacrylic acid is produced from methacrolein at a reaction temperature of about 250 to 400 °C in a fixed bed reactor.

[0003]

A phosphorus-molybdenum-vanadium catalyst is used in a reaction over relatively a long period of time, and its deterioration with the passage of time in the reaction is known. It is desirable that the catalyst is able to retain catalytic activity over a long period stably from the industrial standpoint and economical standpoint. Therefore, producing methods of the catalyst and catalyst formulations have been eagerly improved.

[0004]

Also, there are various suggestions on a method for regenerating the deteriorated catalyst. For example, Patent Document 1 discloses a method for regenerating a catalyst in which a catalyst having deteriorated activity is dispersed in an aqueous medium and treated with a nitrogen-containing hetero-cyclic compound. Patent Document 2 discloses a method for regenerating a used catalyst by the action of an oxidizer or oxidation method, and the dissolving action of an ammonia aqueous solution containing added acetic acid and/or its ammonium salt, and subsequent drying and calcination, wherein the content of a metal component is quantitatively measured, and the metal component is replenished so that this content is returned to its initial value. Both of the methods described in Patent Documents 1 and 2 are methods for regenerating a catalyst removed from a reactor.

[0005]

On the other hand, methods of regenerating a catalyst in a reactor are also variously suggested. For example, Patent Document 3 discloses a method for regenerating a catalyst in which a catalyst having lowered activity is

treated at a temperature of 70 to 240 °C in a gas flow having a water vapor partial pressure of 10 vol% or more. Patent Document 4 discloses a method for regenerating a deteriorated catalyst in a reactor in which a thermal treatment of the catalyst is conducted at a temperature of 300 to 410 °C for 0.5 to 50 hours under flow of an oxidizing gas containing molecular oxygen in an amount of at least 0.1 vol%.

[0006]

Further, Patent Document 5 discloses a method for regenerating a catalyst in which a catalyst composed of a mixed oxide of vanadium and phosphorus used in a method for oxidizing a hydrocarbon having 4 carbon atoms to produce maleic anhydride is allowed to contact with a water vapor in an amount of 0.02 to 30 g per 1 g of the catalyst at 300 to 600 °C. Patent Document 6 discloses a method for regenerating a catalyst in which a molybdenum-vanadium oxidation catalyst having catalytic activity decreased in a cause of use in a process for producing acrylic acid from acrolein or a reaction raw material gas containing acrolein by catalytic oxidation in a vapor phase is thermally treated at a temperature in the range of 300 to 450 °C under flow of a mixed gas containing at least 3 vol% of molecular oxygen and at least 0.1 vol% of water vapor.

[0007]

To prevent deterioration of a catalyst and to use the catalyst stably over a long period is industrially important matter.

[0008]

[Patent Document 1]

Japanese Patent Application Laid-Open No. 60-232247

[Patent Document 2]

Japanese Patent Application Laid-Open No. 6-233938

[Patent Document 3]

Japanese Patent Application Laid-Open No. 58-156351

[Patent Document 4]

Japanese Patent Application Laid-Open No. 6-7685

[Patent Document 5]

Japanese Patent Application Laid-Open No. 8-332387

[Patent Document 6]

Japanese Patent Application Laid-Open No. 6-262081

[0009]

[Problems to be Solved by the Invention]

An object of the present invention is to provide a simple catalyst preserving method having a process for continuously producing an objective product by a vapor phase oxidation reaction using a phosphorus-molybdenum-vanadium catalyst in which deterioration can be prevented before the start of the reaction using a catalyst retained in a reactor or during the stop of the reaction.

[00010]

[Means for Solving the Problems]

The above-mentioned object can be accomplished by the following present inventions.

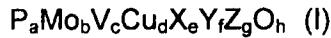
- (1) A method for preserving a catalyst comprising maintaining a phosphorus-molybdenum-vanadium catalyst containing phosphorus, molybdenum and vanadium retained in a reactor under a condition of a water content of 30 mg or less per 1 g of catalyst dry weight, before the start of the reaction or during the stop of the reaction.
- (2) The method for preserving a catalyst according to above-mentioned (1), wherein a retaining temperature of said catalyst is 15 °C or higher and 150 °C or lower and a water concentration in gas in said reactor is 0.5 vol% or less.

(3) The method for preserving a catalyst according to above-mentioned (2), wherein said temperature of the catalyst is retained 15 °C or higher and not higher than 150 °C, and the gas having a water concentration of 0.5 vol% or less and containing substantially no component lowering a catalytic performance is allowed to pass through in said reactor.

(4) The method for preserving a catalyst according to above-mentioned (3), wherein the gas to be passed through in the reactor is an inert gas or oxidizing gas.

(5) The method for preserving a catalyst according to any one of above-mentioned (1) to (4), wherein said phosphorus-molybdenum-vanadium catalyst is a catalyst used in producing methacrylic acid from methacrolein by catalytic oxidation in a vapor phase.

(6) The method for preserving a catalyst according to any one of above-mentioned (1) to (5), wherein said phosphorus-molybdenum-vanadium catalyst is represented by the following formula (I):



wherein, P, Mo, V, Cu and O represent phosphorus, molybdenum, vanadium, copper and oxygen, respectively; X represents at least one element selected from the group consisting of antimony, bismuth, arsenic, germanium, zirconium, tellurium, silver, selenium, silicon, tungsten and boron; Y represents at least one element selected from the group consisting of iron, zinc, chromium, magnesium, tantalum, cobalt, manganese, barium, gallium, cerium and lanthanum; and Z represents at least one element selected from the group consisting of potassium, rubidium and cesium. a, b, c, d, e, f, g and h represent atom ratio of each element, and when b=12, then, a=0.5 to 3, c=0.01 to 3, d=0.01 to 2, e=0 to 3, f=0 to 3, g=0.01 to 3, and h represents atom ratio of oxygen necessary for satisfying atomic valence of each component.

(7) The method for preserving a catalyst according to any one of above-mentioned (1) to (6), wherein said phosphorus-molybdenum-vanadium catalyst is preserved in dark ambient.

[0012]

[Embodiments for Carrying out the Invention]

In a process for continuously producing an objective product using a catalyst filled in a reactor, the catalyst is retained in a reactor in some cases under a condition of not reaction such as from filling of a catalyst to the start of the reaction, or during the stop of operation (during the stop of the reaction) and the like. A phosphorus-molybdenum-vanadium catalyst used, for example, in producing methacrylic acid from methacrolein by catalytic oxidation in a vapor phase shows decrease in catalytic activity in some cases also before the start of the reaction or during the stop of the reaction as described above, in addition to activity decrease and, further, deactivation in the reaction.

[0013]

The inventors of this application have found that a cause for activity decrease of a catalyst before the start of the reaction or during the stop of the reaction is absorption of moisture to the catalyst. It has been also found that a catalyst having activity once decreased by absorption of moisture does not show recovery of activity even if it is simply re-dried in dry air.

[0014]

In the present invention, by maintaining a phosphorus-molybdenum-vanadium catalyst under a condition of a water content of 30 mg or less (including also 0 mg) per 1 g of catalyst dry weight, decrease in activity of a catalyst is prevented before the start of the reaction or during the stop of the reaction, resultantly, the catalyst can be used stably over a long period.

[0015]

For maintaining the water content of a phosphorus-molybdenum-vanadium catalyst in the above-mentioned range, the catalyst retaining temperature and a water content in a gas to be contacted with the catalyst are important.

[0016]

The catalyst retaining temperature is usually not higher than the calcination temperature in catalyst production, preferably not higher than the reaction temperature, more preferably 150 °C or lower. The calcination temperature is usually about 300 to 500 °C, and the reaction temperature is usually about 300 to 400 °C. The catalyst retaining temperature is usually 0 °C or more, preferably 15 °C or more. It is preferable that the catalyst retaining temperature is not so high from the standpoint of thermal stability of a catalyst and economy.

[0017]

The water concentration in gas in a reactor is preferably 1 vol% or less (including also 0 vol%), more preferably 0.5 vol% or less.

[0018]

As the method for maintaining the water concentration in gas in a reactor within the above-mentioned range, there is mentioned, for example, a method in which a gas having a water concentration of 1 vol% or less, preferably 0.5 vol% or less and containing substantially no component lowering catalyst performance is allowed to pass through in the reactor. This method does not require big works, and even if injure of equipments or sealing failure part is present, a possibility of entering of outer air into the reactor is low. As the component lowering catalyst performance, for example, halogens, halogen-containing compounds, sulfur-containing compounds and the like are mentioned.

[0019]

As the gas containing substantially no component lowering catalyst performance to be passed through in the reactor, inert gases, oxidizing gases containing oxygen, and the like are mentioned. Specifically, air, oxygen, nitrogen, combustion gas and the like are mentioned. These gases may be used singly or in admixture of two or more. When oxygen is contained, the oxygen concentration is not particularly restricted, and it is preferably 10 to 30 vol% from the standpoint of economy and safety. As the gas to be passed through in the reactor, air is preferably used from the standpoint of cost.

[0020]

The water concentration in a gas to be passed through in the reactor can be controlled, for example, by lowering once the temperature of the gas and reducing the water concentration in the gas down to saturated vapor amount at this temperature. Plant air and instrument air and the like having small water concentration in gas can also be used as it is.

[0021]

The amount of a gas to be passed through in the reactor is not particularly restricted providing it is an amount preventing outer air from entering into the reactor. The amount of a gas to be passed through in the reactor can be appropriately determined in view of closeness of the reactor, economy, workability and the like.

[0022]

As the method for maintaining the water concentration in gas in the reactor within the above-mentioned range, there is mentioned a method in which the reactor is filled with a gas showing substantially no reactivity having a water concentration of 0.5 vol% or less, then, a closing plate or the like is inserted into piping at the inlet side and outlet side of a gas in the reactor to attain closure, in addition to the above-mentioned method.

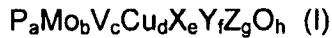
[0023]

In the present invention, it is preferable to make dark ambient in the reactor and preserve a phosphorus-molybdenum-vanadium catalyst in it since deterioration in activity of a catalyst can be suppressed.

[0024]

The phosphorus-molybdenum-vanadium catalyst used in the present invention is not particularly restricted providing it contains phosphorus, molybdenum and vanadium, and a phosphorus-molybdenum-vanadium catalyst used in producing methacrylic acid from methacrolein by catalytic oxidation in a vapor phase gives more excellent results. Particularly, in the case of a phosphorus-molybdenum-vanadium catalyst represented by the following formula (I), more excellent results are obtained.

[0025]



wherein, P, Mo, V, Cu and O represent phosphorus, molybdenum, vanadium, copper and oxygen, respectively; X represents at least one element selected from the group consisting of antimony, bismuth, arsenic, germanium, zirconium, tellurium, silver, selenium, silicon, tungsten and boron; Y represents at least one element selected from the group consisting of iron, zinc, chromium, magnesium, tantalum, cobalt, manganese, barium, gallium, cerium and lanthanum; and Z represents at least one element selected from the group consisting of potassium, rubidium and cesium. a, b, c, d, e, f, g and h represent atom ratio of each element, and when b=12, then, a=0.5 to 3, c=0.01 to 3, d=0.01 to 2, e=0 to 3, f=0 to 3, g=0.01 to 3, and h represents atom ratio of oxygen necessary for satisfying atomic valence of each component.

[0026]

[Examples]

The present invention will be described by examples and comparative examples below, but the scope of the invention is not limited to the examples.

[0027]

In examples, comparative examples and reference examples, "part(s)" mean "part(s) by weight" and "%" means "vol%" unless otherwise stated.

[0028]

The reaction ratio of methacrolein, the selectivity of methacrylic acid, the yield of methacrylic acid and the water content of a catalyst were defined as described below.

[0029]

Reaction ratio (%) of methacrolein = $B / A \times 100$

Selectivity (%) of methacrylic acid = $C / B \times 100$

Yield (%) of methacrylic acid = $C / A \times 100$

Water content of a catalyst (mg/g) = D / E

Here, "A" represents mol number of methacrolein fed, "B" represents mol number of methacrolein reacted and "C" represents mol number of methacrylic acid produced. "D" represents the weight of water in a catalyst (mg), and "E" represents the weight of a catalyst under dry condition, namely, catalyst dry weight (g).

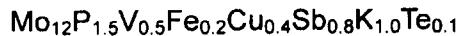
[0030]

Products were analyzed by gas chromatography. The weight of a catalyst after preparation of the catalyst in reference examples, and the weight of a catalyst retained under the same preserving condition in a reactor in examples and comparative examples, was measured. Then, the catalyst was dried and the weight thereof (catalyst dry weight) was measured. A difference between them was used as the weight of water in the catalyst and the water content of the catalyst was calculated according to the above-described formula.

[0031]

<Reference Example 1>

100 parts of ammonium paramolybdate, 2.8 parts of ammonium metavanadate and 4.8 parts of potassium nitrate were dissolved in 100 parts of pure water. While stirring this solution, a solution prepared by dissolving 8.2 parts of 85 wt% phosphoric acid in 10 parts of pure water was added to this, further, a solution prepared by dissolving 1.1 parts of telluric acid in 20 parts of pure water, and 5.4 parts of antimony trioxide were added and the mixture was heated up to 95 °C. To this was added a solution prepared by dissolving 4.5 parts of copper nitrate and 3.8 parts of ferric nitrate in 30 parts of pure water, and the resulted mixture was evaporated to dryness while stirring with heating at 100 °C. The resulted solid was dried at 130 °C for 16 hours, then, molded under press, and thermally treated at 380 °C for 5 hours under air flow to obtain a phosphorus-molybdenum-vanadium catalyst. The element formulation of this catalyst excepting oxygen was as shown below.



The water content of the catalyst was 3.7 mg-H₂O/g-catalyst(dry).

[0032]

This catalyst was filled in a stainless steel reactor having an internal diameter of 16.1 mm and a length of 600 mm, and a reaction gas composed of 6 % of methacrolein, 11 % of oxygen, 30 % of water vapor and 53 % of nitrogen was passed through under normal pressure at a reaction temperature 285 °C for a contact time of 3.8 seconds, performing a vapor phase oxidation reaction. The product was collected and analyzed, as a result, the reaction ratio of methacrolein was 87.8 %, the selectivity of methacrylic acid was 87.5 %, and the yield of methacrylic acid was 76.8 %.

[0033]

<Example 1>

The same catalyst as prepared in Reference Example 1 was filled in the same stainless steel reactor as used in Reference Example 1. Then, air having

a water concentration of 0.3 % was passed through at 0.3 L/Hr per unit catalyst weight (g) while retaining the temperature of a catalyst layer at 20 °C for 10 days. The water content of the catalyst after maintaining for 10 days was 5.6 mg-H₂O/g-catalyst(dry).

[0034]

The same reaction was conducted as in Reference Example 1 using this catalyst. As a result, the reaction ratio of methacrolein was 87.0 %, the selectivity of methacrylic acid was 88.2 %, and the yield of methacrylic acid was 76.7 %.

[0035]

<Example 2>

The same catalyst as prepared in Reference Example 1 was filled in the same stainless steel reactor as used in Reference Example 1. Then, plant air having a water concentration of about 0 % (dew point -35 °C) was passed through at 0.6 L/Hr per unit catalyst weight (g) while retaining the temperature of a catalyst layer at 15 °C for 40 days. The water content of the catalyst after maintaining for 40 days was 3.8 mg-H₂O/g-catalyst(dry).

[0036]

The same reaction was conducted as in Reference Example 1 using this catalyst. As a result, the reaction ratio of methacrolein was 86.6 %, the selectivity of methacrylic acid was 88.1 %, and the yield of methacrylic acid was 76.3 %.

[0037]

<Example 3>

The same catalyst as prepared in Reference Example 1 was filled in the same stainless steel reactor as used in Reference Example 1. Then, air having a water concentration of 0.2 % was passed through at 0.3 L/Hr per unit catalyst weight (g) while retaining the temperature of a catalyst layer at 30 °C for 20

days. The water content of the catalyst after maintaining for 20 days was 4.2 mg-H₂O/g-catalyst(dry).

[0038]

The same reaction was conducted as in Reference Example 1 using this catalyst. As a result, the reaction ratio of methacrolein was 86.2 %, the selectivity of methacrylic acid was 88.6 %, and the yield of methacrylic acid was 76.4 %.

[0039]

<Comparative Example 1>

The same catalyst as prepared in Reference Example 1 was filled in the same stainless steel reactor as used in Reference Example 1. Then, air having a water concentration of 0.9 % was passed through at 0.3 L/Hr per unit catalyst weight (g) while retaining the temperature of a catalyst layer at 15 °C for 16 hours. The water content of the catalyst after maintaining for 16 hours was 44.3 mg-H₂O/g-catalyst(dry).

[0040]

The same reaction was conducted as in Reference Example 1 using this catalyst. As a result, the reaction ratio of methacrolein was 77.4 %, the selectivity of methacrylic acid was 88.2 %, and the yield of methacrylic acid was 68.3 %.

[0041]

<Comparative Example 2>

The same catalyst as prepared in Reference Example 1 was filled in the same stainless reactor as used in Reference Example 1. Then, air having a water concentration of 0.9 % was passed through at 0.3 L/Hr per unit catalyst weight (g) while retaining the temperature of a catalyst layer at 30 °C for 10 days. The water content of the catalyst after maintaining for 10 days was 63.7 mg-H₂O/g-catalyst(dry).

[0042]

The same reaction was conducted as in Reference Example 1 using this catalyst. As a result, the reaction ratio of methacrolein was 60.3 %, the selectivity of methacrylic acid was 80.2 %, and the yield of methacrylic acid was 48.4 %.

[0043]

<Comparative Example 3>

The same catalyst as prepared in Reference Example 1 was filled in the same stainless reactor as used in Reference Example 1. Then, air having a water concentration of 0.9 % was passed through at 0.3 L/Hr per unit catalyst weight (g) while retaining the temperature of a catalyst layer at 15 °C for 16 hours in the same manner as in Comparative Example 1.

[0044]

This catalyst was dried at 280 °C for 5 hours under flow of instrument air having a water concentration of about 0 %. The water content of the catalyst after drying was 4.0 mg-H₂O/g-catalyst(dry).

[0045]

The same reaction was conducted as in Reference Example 1 using this catalyst. As a result, the reaction ratio of methacrolein was 77.7 %, the selectivity of methacrylic acid was 88.5 %, and the yield of methacrylic acid was 68.8 %.

[0046]

<Comparative Example 4>

The same catalyst as prepared in Reference Example 1 was filled in the same stainless steel reactor as used in Reference Example 1. Then, air having a water concentration of 0.9 % was passed through at 0.3 L/Hr per unit catalyst weight (g) while retaining the temperature of a catalyst layer at 30 °C for 10 days in the same manner as in Comparative Example 2.

[0047]

This catalyst was dried at 280 °C for 5 hours under flow of instrument air having a water concentration of about 0 %. The water content of the catalyst after drying was 6.8 mg-H₂O/g-catalyst(dry).

[0048]

The same reaction was conducted as in Reference Example 1 using this catalyst. As a result, the reaction ratio of methacrolein was 62.1 %, the selectivity of methacrylic acid was 81.4 %, and the yield of methacrylic acid was 50.5 %.

[0049]

The results in Reference Example 1, Examples 1 to 3 and Comparative Examples 1 to 4 are shown in Table 1.

[0050]

[Table 1]

	Ref. Ex. 1	Ex. 1	Ex. 2	Ex. 3	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
Retaining conditions								
Catalyst layer temperature (°C)	-	20	15	30	15	30	15	30
Amount of gas passing through (L/Hr)	-	0.3	0.6	0.3	0.3	0.3	0.3	0.3
Water concentration in gas (%)	0.3	about 0	0.2	0.9	0.9	0.9	0.9	0.9
Retaining time	10 days	40 days	20 days	16 hrs	10 days	16 hrs	10 days	
Water content (mg/g)	3.7	5.6	3.8	4.2	44.3	63.7	44.3	63.7
Re-drying conditions								
Temperature (°C)	-	-	-	-	-	-	280	280
Time (Hr)	-	-	-	-	-	-	5	5
Water content after re-drying (mg/g)	-	-	-	-	-	-	4.0	6.8
Reaction results								
Reaction ratio of methacrolein (%)	87.8	87.0	86.6	86.2	77.4	60.3	77.7	62.1
Selectivity of methacrylic acid (%)	87.5	88.2	88.1	88.6	88.2	80.2	88.5	81.4
Yield of methacrylic acid (%)	76.8	76.7	76.3	76.4	68.3	48.4	68.8	50.5

<Reference Example 2>

63.52 parts of ammonium paramolybdate, 1.75 parts of ammonium metavanadate and 7.60 parts of cesium nitrate were dissolved in 200 parts of pure water at 70 °C. While stirring this solution, a solution prepared by dissolving 3.55 parts of 60 wt% arsenic acid in 10 parts of pure water was added to this, further, a solution prepared by dissolving 3.46 parts of 85 wt% phosphoric acid in 10 parts of pure water was added and the mixture was heated up to 95 °C. To this was added a solution prepared by dissolving 2.17 parts of copper nitrate in 10 parts of pure water and a solution prepared by dissolving 2.60 parts of cerium nitrate and 1.30 parts of lanthanum nitrate in 20 parts of pure water sequentially, and the resulted mixture was evaporated to dryness while stirring under heat. The resulted solid was dried at 130 °C for 16 hours, then, molded under press, further, fractured, and fragments having a size of 0.85 to 1.70 mm were separated using a sieve, and thermally treated at 380 °C for 5 hours under air flow to obtain a phosphorus-molybdenum-vanadium catalyst. The element formulation of this catalyst excepting oxygen was as shown below.



The water content of the catalyst was 3.8 mg-H₂O/g-catalyst(dry).

[0051]

This catalyst was filled in a stainless steel reactor having an internal diameter of 16.1 mm and a length of 600 mm, and a reaction gas composed of 6 % of methacrolein, 11 % of oxygen, 30 % of water vapor and 53 % of nitrogen was passed through under normal pressure at a reaction temperature 270 °C for a contact time of 3.6 seconds, performing a vapor phase oxidation reaction. The product was collected and analyzed, as a result, the reaction ratio of methacrolein was 89.8 %, the selectivity of methacrylic acid was 87.6 %, and the yield of methacrylic acid was 78.7 %.

[0052]

<Example 4>

The same catalyst as prepared in Reference Example 2 was filled in the same stainless steel reactor as used in Reference Example 2. Then, air having a water concentration of 0.5 % was passed through at 0.3 L/Hr per unit catalyst weight (g) while retaining the temperature of a catalyst layer at 30 °C for 10 days. The water content of the catalyst after maintaining for 10 days was 15.2 mg- H₂O/g-catalyst(dry).

[0053]

The same reaction was conducted as in Reference Example 2 using this catalyst. As a result, the reaction ratio of methacrolein was 89.5 %, the selectivity of methacrylic acid was 88.0 %, and the yield of methacrylic acid was 78.8 %.

[0054]

<Example 5>

The same catalyst as prepared in Reference Example 2 was filled in the same stainless steel reactor as used in Reference Example 2. Then, air having a water concentration of 0.9 % was passed through at 0.3 L/Hr per unit catalyst weight (g) while retaining the temperature of a catalyst layer at 30 °C for 4 days. The water content of the catalyst after maintaining for 4 days was 28.5 mg- H₂O/g-catalyst(dry).

[0055]

The same reaction was conducted as in Reference Example 2 using this catalyst. As a result, the reaction ratio of methacrolein was 89.1 %, the selectivity of methacrylic acid was 87.8 %, and the yield of methacrylic acid was 78.2 %.

[0056]

<Comparative Example 5>

The same catalyst as prepared in Reference Example 2 was filled in the same stainless steel reactor as used in Reference Example 2. Then, air having a water concentration of 0.5 % was passed through at 0.3 L/Hr per unit catalyst weight (g) while retaining the temperature of a catalyst layer at 10 °C for 1 day. The water content of the catalyst after maintaining for 1 day was 45.3 mg-H₂O/g-catalyst(dry).

[0057]

The same reaction was conducted as in Reference Example 2 using this catalyst. As a result, the reaction ratio of methacrolein was 78.6 %, the selectivity of methacrylic acid was 86.2 %, and the yield of methacrylic acid was 67.8 %.

[0058]

The results in Reference Example 2, Examples 4, 5 and Comparative Example 5 are shown in Table 2.

[0059]

[Table 2]

	Ref. Ex. 2	Ex. 4	Ex. 5	Comp. Ex. 5
Retaining conditions				
Catalyst layer temperature (°C)	-	30	30	10
Amount of gas passing through (L/Hr)	-	0.3	0.3	0.3
Water concentration in gas (%)		0.5	0.9	0.5
Retaining time		10 days	4 days	1 day
Water content (mg/g)	3.8	15.2	28.5	45.3
Re-drying conditions				
Temperature (°C)	-	-	-	-
Time (Hr)	-	-	-	-
Water content after re-drying (mg/g)	-	-	-	-
Reaction results				
Reaction ratio of methacrolein (%)	89.8	89.5	89.1	78.6
Selectivity of methacrylic acid (%)	87.6	88.0	87.8	86.2
Yield of methacrylic acid (%)	78.7	78.8	78.2	67.8

[0060]

[Effects of the Invention]

According to the present invention, in a process for continuously producing an objective product by a vapor phase oxidation reaction using a phosphorus-molybdenum-vanadium catalyst, deterioration before the start of the reaction of a catalyst retained in a reactor or during the stop of the reaction can be prevented by a simple method. As a result, a catalyst can be used stably over a long period.

[Document Name] Abstract

[Summary]

[Problems] It is to provide a simple catalyst preserving method having a process for continuously producing an objective product by a vapor phase oxidation reaction using a phosphorus-molybdenum-vanadium catalyst in which deterioration can be prevented before the start of the reaction using a catalyst retained in a reactor or during the stop of the reaction.

[Means for Solving the Problems] It is to maintain a phosphorus-molybdenum-vanadium catalyst containing phosphorus, molybdenum and vanadium retained in a reactor under a condition of a water content of 30 mg or less per 1 g of catalyst dry weight, before the start of the reaction or during the stop of the reaction.

[Elected Drawing] None